Bibliographic Fields

Document Identity

(19)□□□□□	(19) [Publication Office]
□□□□□□(JP)	Japan Patent Office (JP)
(12)□□□□□□	(12) [Kind of Document]
□□□□□□	Japan Unexamined Patent Publication
(11)□□□□□□	(11) [Publication Number of Unexamined Application]
□□ 2004-234957(P2004-234957A)	Japan Unexamined Patent Publication 2004-234957 (P2004-234957A)
(43)□□□□□	(43) [Publication Date of Unexamined Application]
2004-08-19	2004-08-19

Public Availability

(43)□□□□□	(43) [Publication Date of Unexamined Application]
2004-08-19	2004-08-19

Technical

(54)□□□□□□□	(54) [Title of Invention]
□□□□□□□□□□□□□□□□□□□□□□□□□□□□	**MANUFACTURING METHOD OF LITHIUM SECONDARY BATTERY AND POSITIVE ELECTRODE ACTIVE MATERIAL FOR LITHIUM SECONDARY BATTERY**
(51)□□□□□□□□ 7 □□	(51) [International Patent Classification, 7th Edition]
H01M4/58	H01M4/58
H01M10/40	H01M10/40
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H01M10/40 Z	H01M10/40 Z
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5H029	5H029
5H050	5H050
□F □□□(□□)□	[F Term (For Reference)]
5H029AJ03	5H029AJ03
5H029AK03	5H029AK03
5H029AK19	5H029AK19
5H029AL06	5H029AL06
5H029AL12	5H029AL12
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(21)□□□□□□	(21) [Application Number]
□□ 2003-020540(P2003-020540)	Japan Patent Application 2003-020540 (P2003-020540)

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(22) [Application Date]

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Abstract

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[Problems to be Solved by the Invention]

The;al -LIALO manufacturing method and the;al of anode material and its anode material where content of (2) is high -LIALO lithium secondary battery which uses anode material where content of (2) is high is offered.

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[Means to Solve the Problems]

1. 7 and 0 <= Y <= in 0.5 ranges, element M is metal element of the one kind or more which can become ion of trivalent .) Possessing, you adopt lithium secondary battery 1 which designates that it becomes asfeature. XAs for X and Y which show composition ratio 0Possessing positive electrode 2 and include negative electrode active material negative electrode 3 and nonaqueous electrolyte which include positive electrode active material , Li (X) Al which becomes, as theaforementioned positive electrode active material the;al -LIALO includes (2) crystal (1 -Y) M (Y) O the composition which becomes (2)

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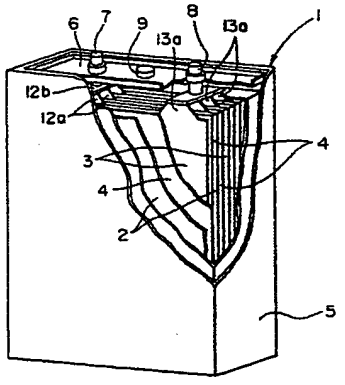
[Selected Drawing]

Figure 1



1：リチウム二次電池
2：正極電極
3：負極電極
4：セパレータ

Claims

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[Claim(s)]

[Claim 1]

1. 7 and 0 <= Y <= in 0.5 ranges, element M is element of the one kind or more which can become ion of trivalent .)

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Possessing, lithium secondary battery . which designates that it becomes as featureXAs for X and Y which show composition ratio 0Possessing positive electrode and include negative electrode active material negative electrode and nonaqueous electrolyte which include positive electrode active material , lixa 11 which becomes, as theaforementioned positive electrode active material the;al -LIALO includes 2 crystal -ymy composition which becomes O2

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[Claim 2]

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1. 3 and 0 <= **W** <= in 0.5 ranges, element L is element of the one kind or more which can become ion of trivalent .). Possessing, lithium secondary battery . which designates that it becomes as featureVAs for v and W composition ratio is shown 0Possessing positive electrode and include negative electrode active material negative electrode and nonaqueous electrolyte which include positive electrode active material , liva 11 which becomes, as theaforementioned positive electrode active material the;ga -LIALO includes 2 crystal -wlw composition which becomes O2

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[Claim 3]

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Possessing positive electrode and include negative electrode active material negative electrode and nonaqueous electrolyte which include positive electrode active material , it becomes, The;al -LIALO Li (X) Al which includes (2) crystal (1 -Y) M (Y) composition and the;ga which become O (2) -LIALO Li (V) Al whichincludes (2) crystal (1 -W) L (W) possessing composition which becomes O (2)as aforementioned positive electrode active material , lithium secondary battery . which designates that itbecomes as feature

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1. 7 and 0 <= **Y** <= in 0.5 ranges, element M and element L are element of one kind or more which can become ion of respective trivalent . X1. 3 and 0 <= W <= 0. 5 and 0 VHowever, as for v, W, X and Y which show composition ratio , 0

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[Claim 4]

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Aforementioned;al -LIAL lixa 11 which includes O2 crystal -ymy lithium secondary battery . which is stated in any of Claim 1 or Claim 3 whichdesignates that average particle diameter of powder of composition which becomes theO2 is 20;mu m or less as feature

□□□□5□

[Claim 5]

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Aforementioned;ga -LIAL liva 11 which includes O2 crystal -wlw lithium secondary battery . which is stated in any of Claim 2 through Claim 4 whichdesignates that average particle diameter of powder of composition which becomes theO2 is 20;mu m or less as feature

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[Claim 6]

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As carbon powder is contained as aforementioned negative electrode , as theaforementioned negative electrode active material metallic lithium being installed in surface , it canhave those which become, lithium secondary battery . which is stated in any of the Claim 1 through Claim 5 which designates that initial discharge is done after battery assembly andbecomes as feature

□□□□7□

[Claim 7]

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As it mixes aluminum alkoxide and lithium compound in addition to organic solvent ,vis-a-vis aforementioned aluminum alkoxide 1mole reacting including water of 3 mole or more , removing aforementioned organic solvent and aforementioned waterafter reaction termination , in making dried matter , said dried matter with temperature of 200*or higher 600* or below 2 hours or more calcining depending, The;al -LIAL manufacturing method . of positive electrode active material for lithium secondary battery which designatesthat positive electrode active material which consists of composition which includes O2 crystal is obtained as feature

□□□□8□

[Claim 8]

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By fact that 550 * exceeding, 2 hours or more it heats aforementioned dried matter with temperature of 600 *or below , the;al -LIAL O2 crystal andthe;ga -LIAL manufacturing method . of positive electrode active material for lithium secondary battery which is stated in Claim 7 which designates that positive electrode active material which consists of composition which includes O2 crystal is obtained as feature

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[Claim 9]

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manufacturing method . of positive electrode active material for lithium secondary battery which is stated in Claim 7 or Claim 8 which designates that it mixes in addition with to aforementioned aluminum alkoxide and aforementioned lithium compound , alkoxide of metal of the any one kind or more of V, Cr , Mn , Co , Ni , Ga , Y, In , la, ND, Gd, Yb and Bi in addition to aforementioned solvent as feature

Specification

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[Description of the Invention]

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[Technological Field of Invention]

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this invention, being a anode material and its manufacturing method for lithium secondary battery and somethingregarding lithium secondary battery , especially, is something regarding manufacturing method of composition which includes lithium secondary battery and Lialo (2) crystal whichdesignate composition which includes Lialo (2) crystal as positive electrode active material .

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[0002]

[Prior Art]

Among lithium secondary battery , as for battery which is called lithium ion secondary battery , lithium ion making use of positive electrode active material and negative electrode active material which intercalation-deintercalation it is a battery' where charge-discharge is done by fact that coming and going it does the lithium ion between positive electrode and negative electrode it is possible.

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When here, desirable condition is listed as positive electrode active material of lithium secondary battery , ithas possessed crystal structure which has acceptable site , lithium ion scattering cando (1) many lithium ion easily inside (2) crystal structure , (3) positive electrode active material itself the toxicity to be little is inexpensive as much as possible with chemically stable ,synthesis of (4) active substance is easy, or other condition can be illustrated.

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[0003]

Presently, Li CoO (2) (Co system) and Li Mn (2) O (4) (Mn system) etc is usedfor positive electrode active material of lithium secondary battery .

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Li CoO (2) designates halite structure type as basic structure , shows layered structure byfact that crystal is warped a little, lithium ion insertion (intercalate) or removal charge-discharge is done by fact that (deintercalation) vis-a-vis this interlayer .

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In addition, Li Mn (2) as for O (4) with spinel structure type, lithium ion of tetrahedron site has participated in charge-discharge .

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When these Li CoO (2) and Li Mn (2) producing O (4), are producedby fact that high temperature firing it does these mixed powder as starting material , Coco(3) powder and Li (2) blend of CO (3) powder and Li (2) making use of CO (3) powder and Mno (2) powder and blend etc.

□0004□

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[0004]

But, Li CoO (2), in order to designate Co which is a strategy substance and as main component with expensive , are times when problem occurs insupply of starting material .

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In addition Li Mn (2) O (4), with 50 *or higher Mn melting in electrolyte solution , is a problem that causes decrease of battery performance .

□□

TRANSLATION STALLEDelectronic equipment secondary battery capacity increase electrode active substance capacity increase cycle lifetime , output characteristic property improvement cost reduction

□0005□

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[0005]

By way, the;ga -LIALO as for (2), as constituent material of

electrolyte holder of molten carbonate fuel cell it is known generally that it uses, but these;ga -LIALO (2)and the;al -LIALO report which uses (2) as positive electrode active material of the lithium secondary battery has not done at present.

Substituting portion of Co which is included in Li CoO (2) in Al , example which uses composition which it acquires as active substance is shown in below-mentioned patent literature 1.

When Li CoO (2) with the;al which possesses same crystal structure -LIALO(2) is included in active substance , it is disclosed in this patent literature 1, butwhen composition ratio y of Al exceeds 0.1, when battery capacity decreases,from fact that statement has done, With this patent literature 1 extremely little;al -LIALO example which with Li CoO (2) uses (2) only is disclosed.

[0006]

By way, in below-mentioned patent literature 1, the;al -LIALO with lialo(2) synthesizing (2) the;al -lialo, it has originated in not beingable to synthesize (2) with alone .

Namely, it can use to production of Lialo (2) solid phase sintering method and the sol-gel method , but when it calcined according to place where inventor of this application experiences concerning solid phase sintering method , making use of lithium carbonate and the aluminum hydroxide , the;ga -lialo synthesis of (2) was possible, but the;al-lialo (2) synthesis is difficult, The;al -LIALO not be able to acquire single phase of (2), the;al-type + the;be -type or the;al -type + the;be -type + the;ga -type those of mixed phase structure only are acquired.

In addition, although the;al -LIALO X-ray diffraction data of (2) it isdisclosed public in database (No of ASTM card . 74 - 2232), as for this data there is a status where actual measurement data is not acquired with synthetic product to be no more than tolast a calculated value .

[0007]

On one hand, in order for there to be a below-mentioned patent literature 2 concerning sol-gel method , report is already done, but as for this inreport to last the;ga -LIALO concerning manufacturing method of (2),description the;al -LIALO concerning (2) is not completely done.

[0008]

[Patent Literature 1]

Japan Unexamined Patent Publication Hei 11- 7958disclosure

[Patent Literature 2]

Japan Patent Application Sho 60- 135720disclosure

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[0009]

[Problems to be Solved by the Invention]

Like above, the;al -type , lialo (2) crystal synthesis beingdifficult to until recently, because the;al -type single phase thing is notacquired, composition to which the;al -type includes lialo (2) crystal concerning applicable whether or not as positive electrode active material for lithium secondary battery was unclear completely.

these inventors this ;al -LIALO invented synthetic method of composition whichincludes (2) crystal mainly in novel , the;al which is synthesized-LIALO when composition which includes (2) crystal is applied to the positive electrode active material of lithium secondary battery , discovered fact that charge-discharge capacity which issuperior is shown, arrived in this invention .

In addition, these inventors when it applies to positive electrode active material the;ga -LIALOconcerning (2) crystal , discovered fact that charge-discharge capacity which issuperior in comparison with conventional Li CoO (2) crystal is shown, arrived in this invention .

As for this invention considering to above-mentioned situation , beingsomething which it is possible, the;al -LIALO (2) or the;ga -LIALO the manufacturing method and the;al of anode material and its anode material where content of (2)is high -LIALO (2) or the;ga -LIALO it designates that lithium secondary battery whichuses anode material where content of (2) is high is offered as the objective .

[0010]

[Means to Solve the Problems]

In order to achieve above-mentioned objective , this invention adopted the configuration below.

1. 7 and 0 <= Y <= in 0.5 ranges, element M is element of the one kind or more which can become ion of trivalent .) Possessing, it designates that it becomes as feature. Furthermore;al -LIALO as for (2) crystal , space group R- 3 m and No. It is a crystal which is displayed with 166. XAs for X and Y which show composition ratio 0Li (X) Al where lithium secondary battery of this invention becomes, possessing positive electrode and include negative electrode active material negative electrode and nonaqueous electrolyte which include positive electrode active material , as aforementioned positive electrode active material the;al -LIALO includes (2) crystal (1 -Y) M (Y) O composition which becomes (2)

[0011]

1. 3 and 0 <= W <= in 0.5 ranges, element L is element of the one kind or more which can become ion of trivalent .) Possessing, it designates that it becomes as feature.

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Furthermore;ga -LIALO as for (2) crystal , space group P4 (1) 2 (1) 2, No. It isa crystal which is displayed with 92. VAs for v and W composition ratio is shown 0In addition Li (V) Al where lithium secondary battery of this invention becomes,possessing positive electrode and include negative electrode active material negative electrode and nonaqueous electrolyte which include positive electrode active material , as aforementioned positive electrode active material the;ga -LIALOincludes (2) crystal (1 -W) L (W) O composition which becomes (2)

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[0012]

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In addition lithium secondary battery of this invention becomes possessing positive electrode andinclude negative electrode active material negative electrode and nonaqueous electrolyte which include positive electrode active material , The;al -LIALO Li (X) Al which includes (2) crystal (1 -Y) M (Y) composition and the;ga which become O (2) -LIALO Li (V) Al whichincludes (2) crystal (1 -W) L (W) possessing composition which becomes O (2)as aforementioned positive electrode active material , it designates that it becomes as feature.

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1. 7 and 0 <= Y <= in 0.5 ranges, element M and element L are element of one kind or more which can become ion of respective trivalent . X1. 3 and 0 <= W <= 0. 5 and 0 VHowever, as for v, W, X and Y which show composition ratio , 0

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[0013]

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As for above-mentioned lithium secondary battery , the;al -type or being somethingwhich uses composition to which the;ga -type includes lialo (2) crystal of any one or both as positive electrode active material , as for this composition atomic weight of the per mole to be small in comparison with lithium composite oxide of conventional Co type or Mn type, at same time electrochemical equivalent of lithium equality to conventional lithium composite oxide above that, Because of that it is something where energy density per weight is high.

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It is possible to raise energy density by fact that this composition is usedfor lithium secondary battery .

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Especially, the;al -LIALO as for lithium secondary battery which designates composition which includes (2) crystal as positive electrode active material , initial discharge capacity much high discharge capacity is acquired in comparison with 470 mAh/g and conventional Li CoO (2).

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In addition, the;ga -LIALO as for lithium secondary battery which designates composition which includes (2) crystal as positive electrode active material , although initial discharge capacity 300 mAh/g and does not reach in the;al -type , high discharge capacity is acquired in the satisfactory in comparison with conventional Li CoO (2).

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In addition, the;al -type and as for lithium secondary battery which designates the composition to which the;ga -type includes lialo (2) crystal as positive electrode active material ,initial discharge capacity becomes 380 mAh/g , the;al -type , the;ga -type discharge capacity of extent of intermediate is almost acquired.

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In case of this , high discharge capacity is acquired in satisfactory incomparison with conventional Li CoO (2).

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[0014]

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1.7 Range is good. If it is a range which drives, the;al -type or the;ga -type canraise stability of crystal structure of lialo (2) crystal , it is possible toinsert lithium ion and removal smoothly. Raising from stability of joining structure , in order charge-discharge cycle property toimprove, when 0.5 <= v <= 1.250.5 <= X <= it puts range of vand X respectively in 1.66 ranges, it is good. X1.3 0VIn addition, composition ratio v of lithium (Li) in above-mentioned composition ,X respectively 0

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[0015]

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In addition, when portion of Al in Lialo (2) crystal issubstituted in element m or element l, it is possible furthermore toraise stability of crystal structure of Lialo (2) crystal , from charge-discharge cycle property improves.

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Here, element M and element L, with element of any one kind or more of V, the Cr , Mn , Co , Ni , Ga , Y, In , la, ND, Gd, Yb and Bi , are metal element which can become ion of respective trivalent .

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These element M, composition ratio w of L, as for Y exceeding 0, range of 0.5 or less is desirable.

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W, when Y exceeds 0.5, because charge-discharge capacity per weight decreases, itis not desirable.

□0016□

[0016]

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In addition, lithium secondary battery of this invention , with lithium secondary battery which is statedfirst, aforementioned;al -LIALO Li (X) Al which includes(2) crystal (1 -Y) M (Y) designates that average particle diameter of powder of the composition which becomes O (2) is 20;mu m or less as feature.

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In addition lithium secondary battery of this invention , with lithium secondary battery which is statedfirst, aforementioned;ga -LIALO Li (V) Al which includes(2) crystal (1 -W) L (W) designates that average particle diameter of powder of the composition which becomes O (2) is 20;mu m or less as feature.

□0017□

[0017]

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It is possible to raise charge-discharge capacity , according to

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this lithium secondary battery , the;al-type or by designating average particle diameter of powder of composition to whichthe;ga -type includes lialo (2) crystal as 20;mu m or less .

Furthermore average particle diameter in this specification is median diameter which with laser diffraction is acquired with particle size distribution measurement .

[0018]

In addition as for lithium secondary battery of this invention , as with lithium secondary battery which isstated first, carbon powder is contained as aforementioned negative electrode , asaforementioned negative electrode active material metallic lithium being installed in surface , itcan have those which become, it designates that initial discharge is doneafter battery assembly and becomes as feature.

[0019]

According to this lithium secondary battery , it is possible to insert in composition whichby fact that initial charging it does metallic lithium which is installed in the negative electrode includes Lialo (2) crystal because of this improving, to raise charge-discharge capacity it is possible lithium content of this said composition .

[0020]

In next, manufacturing method of positive electrode active material for lithium secondary battery of this invention as it mixes aluminum alkoxide and lithium compound in addition to organic solvent , vis-a-vis theaforementioned aluminum alkoxide 1mole reacting including water of 3 mole or more , removingaforementioned organic solvent and aforementioned water after reaction termination ,making dried matter , said dried matter with temperature of 200 *or higher 600* or below 2 hours or more calcining depending, The;al -LIALO it designates that positive electrode active material which consists of composition which includes (2) crystal is obtained as feature.

Furthermore completely is not included the;al which -type single phase lialo(2) crystal is acquired the;ga -type by heating above-mentioned dried matter with temperature of 200 *or higher 550* or below .

[0021]

manufacturing method of positive electrode active material for this lithium secondary battery , reacting, designates aluminum alkoxide and lithium compound and water as dried matter of gel , obtains the positive electrode active material which contains Lialo (2) crystal by fact that this dried matter iscalcined, 200 * - 600 * it calcines relatively low temperature by fact that with manufacturing method , it is possible with so-called sol-gel method , to make sintering temperature low,

The;al -LIALO (2) crystal can be synthesized.

Especially, the;al which synthesis makes difficult from until recentlyby designating sintering temperature as 200 *or higher 550* or below , -LIALO composition whichincludes only (2) crystal can be acquired.

□0022□

[0022]

In addition manufacturing method of positive electrode active material for lithium secondary battery of this invention , with manufacturing method of positive electrode active material for lithium secondary battery which is stated first, by thefact that 550 * exceeding, 2 hours or more it heats aforementioned dried matter with temperature of 600 *or below , the;al -LIALO (2) crystal and the;ga-LIALO designates that positive electrode active material which contains (2) crystal isobtained as feature.

□0023□

[0023]

According to manufacturing method of positive electrode active material for this lithium secondary battery , by fact that550 * exceeding, it heats aforementioned dried matter with temperature of600 *or below , the;al -type and composition to which the;ga -type includes lialo (2) crystal of both simultaneously is acquired.

□0024□

[0024]

In addition manufacturing method of positive electrode active material for lithium secondary battery of this invention with the manufacturing method of positive electrode active material for lithium secondary battery which is stated first, designatesthat it mixes in addition to with aforementioned aluminum alkoxide and theaforementioned lithium compound , alkoxide of metal of any one kind or more of V, the Cr , Mn , Co , Ni , Ga , Y, In , la, ND, Gd, Yb and Bi in addition toaforementioned solvent as feature.

□0025□

[0025]

According to manufacturing method of positive electrode active material for this lithium secondary battery , because theabove-mentioned metal alkoxide is added to other than aluminum alkoxide and theaforementioned lithium compound , it is possible to substitute portion of the Al of Lialo (2) crystal in above-mentioned metal , positive electrode active material where stability of crystal structure of Lialo (2) crystal improves, issuperior in charge-discharge cycle property can be acquired.

Namely, sintering temperature to be acquired 200 - 550 * in range, the;al -LIALO Li (X) Al which includes (2) crystal (1 -Y) M (Y) powder of composition which becomes O (2), sintering temperature 550 - 600 * in range, In range where the;al -LIALO Li (X) Al which includes the(2) crystal (1 -Y) M (Y) blend of composition which becomes O (2) and the;ga-LIALO Li (V) Al which includes (2) crystal (1 -W) L

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(W) the composition which becomes O (2) is acquired, sintering temperature 600 * exceeds, The;ga -LIALO Li (V) Al which includes (2) crystal (1 -W) L (W) composition which becomes O (2) is acquired.

□□□

1. 7 and 0 <= Y <= in 0.5 ranges, element M and element L are element of one kind or more which can become ion of respective trivalent . X1. 3 and 0 <= W <= 0. 5 and 0 VFurthermore v, W, X and Y which show composition ratio in theabove-mentioned each composition formula respectively 0

□0026□

[0026]

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[Embodiment of the Invention]

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Below, referring to drawing , you explain embodiment of this invention .

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one example of lithium secondary battery which is a embodiment of this invention is shown in the Figure 1 .

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this lithium secondary battery 1 being something which is called so-called angular type , configuration is done positive electrode of plural (electrode) 2... with, with negative electrode 3* and positive electrode 2 of plural and separator 4* and nonaqueous electrolyte (nonaqueous electrolyte) which are respectivelyarranged between negative electrode 3 as main component .

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positive electrode 2*, negative electrode 3* and separator 4* and nonaqueous electrolyte are stored up in battery case 5 whichconsists of stainless steel etc.

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And sealing plate 6 is installed in upper part of battery case 5.

□□

safety valve 9 which prevents internal pressure rise of battery is provided almost in center of this sealing plate 6.

□□□

It can use to separator 4, nonwoven fabric etc which consists of polyethylene , polypropylene or other porosity polymeric material film , glass fiber , various polymer fiber .

□0027□

[0027]

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positive electrode tab 12* is formed by one end of positive electrode 2*, positive electrode tab 12 a... the said positive electrode tab 12 a... positive electrode lead 12 b which hitch is done is installed in the upper part .

□□□

positive electrode terminal 7 which penetrates sealing plate 6 is installed in this positive electrode lead 12 b.

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In same way, negative electrode tab 13 a... is formed in one end of negative electrode 3*,negative electrode tab 13 a... said negative electrode tab 13 a... negative electrode lead 13 b which hitch is done isinstalled in upper part .

□□□

negative electrode terminal 8 which penetrates sealing plate 6 is installed in this negative electrode lead 13 b.

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Due to above-mentioned configuration , it is designed in such a way that itcan remove current from positive electrode terminal 7 and negative electrode terminal 8.

□0028□

[0028]

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As shown next in Figure 2 , negative electrode 3, on negative electrode collector 3 a and this negative electrode collector 3 awhich consist of Cu foil etc configuration is done from negative electrode film 3 b which film formation is done.

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Aforementioned negative electrode tab 13 a protruding doing in one end of negative electrode collector 3 a,it is formed.

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negative electrode film 3 b is formed, for example graphite or other negative electrode active material powder and polyvinylidene fluoride or other binder being mixed.

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Furthermore when carbon black or other conduction aid powder is added to negative electrode membrane 3 b, it is.

□0029□

[0029]

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As negative electrode active material , pyrolysate or other various carbon material of coke , amorphous carbon , graphitized carbon fiber , various polymeric material canbe used for other than graphite .

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In addition to other than carbon material , is possible also fact that metallic lithium , lithium and various metal oxide etc which are represented in alloy , tin ofvarious metal are used.

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metallic lithium and alloy are good even with those of foil not just powder always.

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In addition, poly tetrafluoroethylene , polyimide etc can be used for other than polyvinylidene fluoride , as binder of negative electrode 3.

□0030□

[0030]

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Furthermore, when above-mentioned various carbon material are used as the negative electrode active material , you can use attachment metallic lithium in surface of negative electrode film 3 bwhich consists of these carbon material as negative electrode .

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metallic lithium which is used here be able to use things such as powder and thin band or other various shape , these should have been pasted together in surface of negative electrode film 3 b.

□0031□

[0031]

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positive electrode 2, positive electrode collector which consists of for example Al foil etc (current collector) to 2 A and on positive electrode collector 2 a positive electrode film which film formation is done (electrode film) configuration is done from2 B.

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Aforementioned positive electrode tab 12 a protruding doing in

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one end of positive electrode collector 2 a,it is formed.

As for positive electrode membrane 2 b, solid component and binder being mixed, beingsomething which formed in film , at least positive electrode active material powder (electrode active substance) and the conduction aid powder is included in solid component .

[0032]

As and shown in Figure 2 , positive electrode film 2 b and negative electrode film 3 b through the separator 4, it is opposed.

Furthermore, in order to make explanation simple regarding Figure 2 ,each current collector 2 a, each electrode film 2 b, shape which 3 B film formation is done hasbeen shown in one surface of 3 A, but each electrode film 2 b, 3 B each current collector 2 a, thefact that film formation it is possible to do is of course in both surfaces of3 A.

[0033]

In addition, the;al -lialo Li (X) Al which includes (2) crystal (1 -Y) M (Y) powder of composition which becomes O (2) can be used as positive electrode active material which is included in positive electrode membrane 2 b.

In addition the;ga -LIALO Li (V) Al which includes (2) crystal (1 -W) L (W) it is possible also as positive electrode active material , to use powder of composition which becomes O (2).

Furthermore, the;al -LIALO Li (X) Al which includes (2) crystal (1 -Y) M (Y) blend of powder of composition which becomes O (2)and the;ga -LIALO Li (V) Al which includes (2) crystal (1 -W) L(W) powder of composition which becomes O (2) can be used as positive electrode active material .

Here,;al -LIALO as for (2) crystal , space group R- 3 m and No. With crystal which is displayed with 166, in addition the;ga -LIALO as for (2) crystal , space group P4 (1) 2 (1) 2, No. It is a crystal which is displayedwith 92.

1. 7 and 0 <= Y <= in 0.5 ranges, element M and element L are element of one kind or more which can become ion of respective trivalent . X1. 3 and 0 <= W <= 0. 5 and 0 VV, W, X and Y which show composition ratio in above-mentioned each composition formula respectively 0

[0034]

As for lithium secondary battery of this embodiment , the;al -type or being something whichuses composition to which the;ga -type includes lialo (2) crystal of any one or both as positive electrode active material , as for this composition atomic weight of per mole to besmall in comparison with lithium composite oxide of conventional Co type or Mn type, at thesame time electrochemical equivalent of lithium equality to conventional lithium composite oxide above that, It is

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something where energy density per weight is high.

By fact that this composition is used for positive electrode active material , it is possible toraise energy density of lithium secondary battery .

Especially, it is something whose it is possible the;al -LIALO (2) crystal Li CoO (2) with to have had similar layer halite structure , to insert the lithium ion and removal easily.

Because of this , the;al -LIALO by fact that it uses composition which includes (2) crystal as positive electrode active material , much high discharge capacity can beacquired in comparison with conventional Li CoO (2).

In addition, the;ga -LIALO as for composition which includes (2) crystal , although charge-discharge capacity does not reach in the;al -type , high discharge capacity is acquired in satisfactory in comparison with Li CoO (2).

In addition the;ga -LIALO composition which includes (2) crystal canacquire cycle property which is superior in comparison with the;al -type .

Furthermore, the;al -type and as for composition to which the;ga -type includes lialo (2) crystal , the;al -type , the;ga -type discharge capacity of extent of intermediate is almost acquired.

In case of this , high discharge capacity is acquired in satisfactory incomparison with conventional Li CoO (2).

[0035]

1.7 Range is good. If it is a range which drives, the;al -type or the;ga -type canraise stability of crystal structure of lialo (2) crystal , it is possible toinsert lithium ion and removal smoothly. Raising from stability of joining structure , in order charge-discharge cycle property toimprove, when 0.5 <= v <= 1.250.5 <= X <= it puts range of vand X respectively in 1.66 ranges, it is good. X1.3 0Vcomposition ratio v of lithium (Li) in above-mentioned composition , Xrespectively 0

[0036]

When composition ratio v and X are 0 respectively, to become state where lithium is not completely included in positive electrode active material , because itdoes not function as lithium secondary battery it is not desirable.

In addition, composition ratio v being 1.3 or greater , when composition ratio x is 1.7 or greater ,because the;al -type , the;ga -type synthesis of lialo (2) crystal becomes difficult, it is not desirable.

[0037]

In addition, when the;al -type and the;ga -type portion of Al in lialo (2) crystal is substituted in element m and element l, itis possible furthermore to raise stability of crystal structure of lialo(2) crystal , from charge-discharge cycle property

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improves.

Here, element M and element L, with element of any one kind or more of V, the Cr , Mn , Co , Ni , Ga , Y, In , la, ND, Gd, Yb and Bi , are element which can become ion of respective trivalent .

When you think from viewpoint of energy density , those where atomic weight issmall as substitute element are good.

These element M, composition ratio w of L, as for Y exceeding 0, range of 0.5 or less is desirable.

When composition ratio w and Y respectively exceed 0.5, because charge-discharge capacity per composition weight decreases, it is not desirable.

[0038]

In addition, the;al -LIALO Li (X) Al which includes (2) crystal (1 -Y) M (Y) as for average particle diameter of powder of composition which becomesO (2) it is desirable to be 20;mu m or less .

In same way, the;ga -LIALO Li (V) Al which includes the(2) crystal (1 -W) L (W) it is desirable also for average particle diameter of powder of composition which becomes O (2) to be 20;mu m or less .

By fact that average particle diameter of powder of each composition is designated as20;mu m or less , it is possible to raise from charge-discharge capacity .

[0039]

In addition, as positive electrode active material , the;al -LIALO Li (X) Al whichincludes (2) crystal (1 -Y) M (Y) case where blend of powder of composition which becomes O (2) and the;ga -LIALO Li (V) Al which includes (2) crystal (1 -W) L (W) powder of composition whichbecomes O (2) is used, When charge-discharge cycle property is seriously considered, when it makes many, the;ga-type content in comparison with the;al -type , when charge-discharge capacity isseriously considered, it makes many the;al -type content incomparison with the;ga -type it is good.

Especially, if even with when charge-discharge capacity is seriously considered,the;al -LIALO the;ga of trace -LIALO it tries to include (2) crystal in (2) crystal , cycle property it can improve.

In case of this , the;ga in positive electrode active material it is good for -type todesignate blend ratio as 20 mass % or greater .

[0040]

In addition, it is good adding polyaniline , polypyrrole , polythiophene , poly imidazole or other conductive polymer material to above-mentioned positive electrode active

material ,when especially polyaniline is added, it is good.

As for these conductive polymer material because in electrochemically stability, furthermore it issuperior in electronic conductivity , resistance of positive electrode film 2 b is decreased by thefact that conductive polymer material is added, internal impedance of battery decreases andthere is an effect to which charge-discharge capacity improves.

As for composition ratio of polyaniline or other conductive polymer material in positive electrode active material , range of 0.1 mass % or greater 5mass % or less isdesirable.

Because under 0.1 mass % addition effect of conductive polymer material which descriptionabove is done you cannot see composition ratio , not to be desirable, when the composition ratio exceeds 5 mass % , because electronic conductivity inhibition is done with the excessive sheath of conductive polymer material , it is not desirable.

[0041]

Next, it is desirable to use carbon black , acetylene black , graphite , carbon fiber or other carbon material , as conduction aid which is includedin positive electrode membrane 2 b.

In addition it is desirable to use polyvinylidene fluoride , poly tetrafluoroethylene , polyimide or other polymer binder , as binder .

In addition it is desirable to use metal foil , metal mesh , expanded metal etc, as positive electrode collector 2 a, inaddition these material Al , ti and stainless steel etc are desirable.

[0042]

As for composition ratio of positive electrode membrane 2 b, positive electrode active material 60 - 90 weight% , conduction aid 5 - 20 mass % , binder range of 5 - 20 mass % are desirable.

[0043]

Those which melt one, two or more kinds of solute which consists of CF (3) SO(2) (2) N or other lithium salt can be used. Next in mixed solvent which mixes for example ethylene carbonate , butylene carbonate or other cyclic carbonate ester and dimethyl carbonate , methylethyl carbonate , diethyl carbonate or other linear carbonate ester nonaqueous electrolyte (nonaqueous electrolyte) as,Lipf (6), Libf (4), Liasf (6), Liclo (4), Licf (3) So(3), Li

[0044]

In addition, replacing to above-mentioned nonaqueous electrolyte , it is possiblealso to use solid electrolyte (nonaqueous electrolyte).

As solid electrolyte , polyethylene oxide or other lithium ion conduction polymer which contains above-mentioned solute

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andimpregnating above-mentioned nonaqueous electrolyte in polyethylene oxide , polyvinylidene fluoride , polyacrylonitrile or other polymer matrix , gel electrolyte etcwhich becomes you can use.

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[0045]

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lithium secondary battery 1 of this embodiment is produced, first, it mixes powder of the positive electrode active material with carbon black or other conduction aid , this blend , it adds to NMP or other dispersion medium where beforehand polyvinylidene fluoride or other binder and polyaniline are melted and makes slurry , this slurry the application after doing, adding heat removal it does dispersion medium in positive electrode collector with doctor blade method , etc it produces positive electrode 2 by compressing with the press etc.

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Next, it mixes powder of negative electrode active material with according to need carbon black or other conduction aid , this blend , itadds to NMP or other dispersion medium where polyvinylidene fluoride or other binder is melted beforehand and makes the slurry , this slurry application after doing, adding heat removal it does the dispersion medium in negative electrode collector with doctor blade method , etc it produces negative electrode 3 bycompressing with press etc.

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[0046]

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And, sequential laminating positive electrode 2 and separator 4 and negative electrode 3, itinserts in battery case 5, pouring liquid does nonaqueous electrolyte next, next connects the sealing plate 6 to battery case 5.

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lithium secondary battery of this embodiment is acquired this way.

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[0047]

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In addition, metallic lithium being installed in surface of negative electrode 3, case lithium secondary battery which becomes is produced, positive electrode 2 and separator 4 and the metallic lithium equipped negative electrode sequential laminating, it inserts in battery case 5,pouring liquid does nonaqueous electrolyte next, next connects sealing plate 6 to battery case 5.

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After that, it moves to positive electrode 2 by doing initial discharge , with metallic lithium of negative electrode 3surface as state of lithium ion .

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lithium ion which reaches to positive electrode 2 the;al -type or the;ga -type isinserted into lialo (2) crystal .

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With this initial discharge , Li (X) Al (1 -Y) M (Y) O (2) or Li (V) Al (1 -W) L (W) composition ratio v of Li which is displayed with composition formula ofO (2), value of X improves.

this way, it is possible to insert in composition which by factthat initial discharge it does metallic lithium which is installed in negative electrode 3 includes Lialo (2) crystal lithium content of this said composition improves because ofthis, it is possible to raise charge-discharge capacity .

Therefore, when metallic lithium is installed in negative electrode 3, lithium content of the positive electrode active material beforehand it should have decreased.

As for composition which includes Lialo (2) crystal where lithium content islittle it is possible, productivity of lithium secondary battery can improve to make the synthesis time relatively short.

Furthermore in order Li (X) Al (1 -Y) M (Y) O (2) or Li (V) Al (1 -W) L (W) composition ratio v of Li which is displayed with the composition formula of O (2), for value of X respectively to become 1.7 and1.3, when it is synthesized in initial stage , it is not necessary toinstall Li foil in negative electrode .

[0048]

Next, manufacturing method of positive electrode active material of this embodiment is explained.

First, aluminum alkoxide and lithium compound are prepared as starting material .

As embodiment of aluminum alkoxide , carbon number of aluminum methoxide , aluminum ethoxide , aluminum isopropoxide , aluminum normal propoxide or other alkyl group can use those of 1 -10 extent .

In addition lithium chloride , lithium bromide , lithium iodide , lithium fluoride , lithium nitrate , lithium hydroxide , lithium carbonate , lithium citrate etc can be used as lithium compound .

[0049]

Furthermore, when portion of Al Li (X) Al which issubstituted in metal element M or L (1 -Y) M (Y) O (2) or Li (V) Al (1 -W) L(W) composition which becomes O (2) is obtained, adding alkoxide of the metal element M or L (V, metal of any one kind or more of Cr , Mn , Co , Ni , Ga , Y, In , la, ND, Gd, Yb and Bi) as starting material , it is necessary to use.

As alkoxide in this case, carbon number of methoxide , ethoxide , isopropoxide , normal propoxide or other alkyl group can use those of 1- 10 extent .

[0050]

Next, throwing these starting material to organic solvent , it mixes.

If furthermore proportion of these starting material , when for example Li (X) Al (1 -Y) M(Y) composition which becomes O (2) is obtained, in order mole ratio of the lithium and aluminum and element M which are included in starting material the Li :Al : m=x: to become (1 -Y):y, you should have adjusted.

In addition, when Li (V) Al (1 -W) L (W) composition which becomes O(2) is obtained, in order mole ratio of lithium and aluminum and the element M which are included in starting material Li :Al : m=v: to become the(1 -W):w, if you should have adjusted.

1. 7 and 0 <= Y <= they are 0.5 ranges. X1. 3 and 0 <= W <= 0. 5 and 0 VFurthermore range of v, W, X and Y respectively 0

[0051]

As for organic solvent where starting material is thrown, aluminum alkoxide and those towhich can melt metal M or L alkoxide are desirable, can use the methanol , ethanol , isopropanol , normal propanol , butanol , pentanol , hexanol or other alcohols , hexane , heptane , octane or other straight chain paraffin type hydrocarbon , cyclic paraffin type hydrocarbon , unsaturated hydrocarbon , ketones , ethers etc concretely.

[0052]

Next, water is added to organic solvent which throws starting material .

aluminum alkoxide and metal M or L alkoxide hydrolysis (Reaction) by fact thatwater is added.

As for addition quantity of water, it is good to make range of 3 mole or more 20mole or less ,vis-a-vis aluminum alkoxide 1mole .

When quantity of water is under 3 mole , aluminum alkoxide etc not todo hydrolysis of perfection, in addition because the;be -LIALO (2) crystal forms after calcining, it is not desirable.

In addition when quantity of water exceeds 20 mole , becauseit means to require lengthy in removal process of water and organic solvent which are done after this it is not desirable.

[0053]

Adding water, after reacting in fully , it removes waterand organic solvent with thermal drying or natural drying .

dried matter of gel is acquired by fact that water and the organic solvent are removed.

Because dried matter of gel which it acquires bulk density is low, itis desirable with objective which raises bulk density to compress withhigh-temperature hydrostatic press etc.

[0054]

□□

Next, it calcines 2 hours or more with temperature of 200 *or higher 600* or below vis-a-vis the dried matter of this gel .

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The;al -LIALO composition which includes (2) crystal is acquired bycalcining.

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When sintering temperature is relatively low temperature of 200 *or higher 550* or below , when most all of thelialo (2) crystal which is included in composition the;al -lialo become the(2) crystal , sintering temperature exceeds 550 *, the;al -lialo the;ga -lialo (2) crystal forms to other than (2) crystal .

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When sintering temperature exceeds 600 *, the;al -LIALO (2) crystal is notcompletely formed, the;ga -type single phase composition is acquired.

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Furthermore because sintering temperature is formed 200 * at under the;be which islacking in electrochemical activity -LIALO (2) crystal , it is not desirable.

□0055□

[0055]

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In addition if sintering time is 2 hours or more , the;al -type and the;ga -type can calcine necessary and sufficient in formation of lialo (2) crystal .

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When sintering time is under 2 hours , because the;be -LIALO (2) crystal isformed, it is not desirable.

□□

In addition, as for sintering time there is not a especially upper limit . When it is an excessive lengthy , because cost of calcining increases,when it makes 96 hours or less, it is good.

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In addition as for atmosphere of calcining, it is desirable to do in atmosphere .

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Because composition which it acquires, being sintered by calcining, ithas become massive, this powder fragment doing with ball mill or other mill , average particle diameter makes powder of 20;mu m or less .

□0056□

[0056]

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Like above, by fact that sintering temperature is designated as 200 *or higher 550* or below ,the;al -LIALO Li (X) Al which includes only (2) crystal (1 -Y) M(Y) composition which becomes O (2) is acquired.

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In addition, by fact that 550 * exceeding, it puts sintering temperature inrange of 600 *or below , the;al -LIALO Li (X) Al which includes(2) crystal (1 -Y) M (Y) blend of composition which becomes O (2) andthe;ga -LIALO Li (V) Al which includes (2) crystal (1 -W) L (W) composition which becomes O (2) is acquired.

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Furthermore, when sintering temperature exceeds 600 *, the;ga -LIALO Li (V) Al which includes only (2) crystal (1 -W) L (W) composition which becomesO (2) is acquired.

□0057□

[0057]

manufacturing method of positive electrode active material for lithium secondary battery of this embodiment, reacting,designates aluminum alkoxide and lithium compound and water as dried matter of the gel, the;al -LIALO obtains positive electrode active material which contains (2) crystal byfact that it calcines this dried matter, with so-called sol-gel method with manufacturing method, itcan synthesize lialo (2) crystal with calcining relatively low temperature.

Especially, the;al which synthesis makes difficult from until recentlyby designating sintering temperature as 200 *or higher 550* or below, -LIALO composition whichincludes only (2) crystal can be acquired.

In addition, by fact that 550 * exceeding, it heats dried matter of gel with temperature of 600 *or below, the;al -type and it canacquire composition to which the;ga -type includes lialo (2) crystal of both simultaneously.

[0058]

Furthermore, because to of aluminum alkoxide and lithium compound other than element Mor metal alkoxide of element L is added, portion of Al of Lialo(2) crystal element m or it is possible to substitute in element l, the positive electrode active material where stability of crystal structure of Lialo (2) crystal improves, issuperior in charge-discharge cycle property can be acquired.

[0059]

[Working Example(s)]

(Working Example 1)

Throwing to ethanol with mole ratio which shows Lino (3) in the Table 1, it mixed, hydrolysis it did furthermore in order to become the aluminum ethoxide per mole 3mole or more, water to in addition. OC (2) H (6) (3) with lithium nitrate Al aluminum ethoxide

In order that next, water and ethanol are removed from reaction product after hydrolysis, 80 * with 1 week standing doing, it dried.

Next, dried matter of gel after drying powder fragment was done with the agate mortar, milled product after forming with hydrostatic press method, in atmosphere, 200 -1100 * with temperature range 1 - 96 hours was calcined with condition whichis kept.

As shown in Table 1 pyrolysate which it acquires by powder fragment doingwith wet ball mill method, composition of this invention Example 1, 3~18 and Comparative Example 1~6 was acquired.

In Table 1, case where each composition is obtained lithium which isa proportion of starting material (Li) with mole ratio and sintering condition of aluminum (Al)are shown in every

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composition .

□00060□

[0060]

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It measured particle diameter vis-a-vis composition which it acquires.

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It did grain size measurement with laser diffraction , particle diameter made median diameter which wassought with laser diffraction .

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In addition, produced phase which is included in composition vis-a-vis the composition which is acquired, by X-ray diffraction , identification was done.

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measurement result of particle diameter and identification result result of produced phase are shownin Table 1 .

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In addition in Figure 3 , X-ray diffraction result of composition (this invention Example 5 , 8, 10, 11) of part isshown.

□00061□

[0061]

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Furthermore, composition of Comparative Example 9 was synthesized those which inorder for mole ratio of Li /Al to become with 1.0, mix powder of lithium carbonate and aluminum oxide , 500 * with by 12 hours calcining.

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Result of X-ray diffraction of composition which it acquires is shown in the Figure 4 .

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Furthermore and, it designated quantity of water as 3 mole vis-a-vis aluminum ethoxide , 500 * with other than thing which 12 hourscalcines it synthesized with as similar to this invention Example 1 , 3~18 and Comparative Example 1~6,synthesized composition of Comparative Example 10.

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Result of X-ray diffraction of composition which it acquires is shown in the Figure 5 .

□00062□

[0062]

□□ 1□

[Table 1]

□00063□

[0063]

Li/Al モル比	焼成条件		生成相 (X線回折による同定相)	平均粒径 (μm)	初期放電容量 (mAh/g)	
	焼成温度 (℃)	保持時間 (時間)				
1.0	150	12	β-$LiAlO_2$ α-Li AlO_2	1以下	50	比較例 1
1.0	200	12	α-$LiAlO_2$	1以下	200	本発明例 1
1.0	500	1	β-$LiAlO_2$ α-$LiAlO_2$	1以下	50	比較例 2
1.0	500	2	α-$LiAlO_2$	1以下	—	本発明例 3
1.0	500	6	α-$LiAlO_2$	1以下	—	本発明例 4
1.0	500	12	α-$LiAlO_2$	1以下	470	本発明例 5
1.0	500	24	α-$LiAlO_2$	1以下	—	本発明例 6
1.0	550	12	α-$LiAlO_2$	1以下	450	本発明例 7
1.0	600	12	α-$LiAlO_2$ γ-$LiAlO_2$	1以下	380	本発明例 8
1.0	700	12	γ-$LiAlO_2$	1以下	300	本発明例 9
1.0	1000	12	γ-$LiAlO_2$	1以下	300	本発明例 10
1.0	1100	12	γ-$LiAlO_2$	1以下	290	本発明例 11
1.25	500	12	α-$LiAlO_2$	1以下	—	本発明例 12
1.25	1000	24	γ-$LiAlO_2$	1以下	300	本発明例 13
1.3	500	12	α-$LiAlO_2$	1以下	—	本発明例 14
1.3	1000	24	γ-$LiAlO_2$ 不明ピーク	1以下	—	比較例 3
1.3	1000	96	γ-$LiAlO_2$	1以下	—	木発明例 15
1.35	500	12	α- $LiAlO_2$	1以下	—	本発明例 16
1.35	1000	24	γ-$LiAlO_2$ 不明相	1以下	—	比較例 4
1.67	500	24	α-$LiAlO_2$	1以下	470	本発明例 17
1.7	500	24	α- $LiAlO_2$ 不明相	1以下	—	比較例 5
1.7	500	96	α- $LiAlO_2$	1以下	—	本発明例 18
1.75	500	96	α- $LiAlO_2$ 不明相	1以下	—	比較例 6

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Way it shows in Table 1 , when sintering temperature 150 * with it is low, when(Comparative Example 1) and retention time 1 hour it is short, in (Comparative Example 2), the;be -LIALO (2)had formed.

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The;al -LIALO (2) had formed regardless of mole ratio of Li and Al retention time sintering temperature 200 * - 550 * concerning thing(this invention Example 1 , 5, 7, 1 2, 1 4, 16) of range in 12 hours, in addition, as shown in Table 1 and the Figure 3 .

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Furthermore, as shown in Table 1 and Figure 3 , sintering temperature the;ga-LIALO (2) had formed concerning thing (this invention example 9 and 1 0, 1 1, 1 3 and 15, Comparative Example 3, 4) of 700 *or higher .

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Furthermore concerning Comparative Example 3 and 4 , result of X-ray diffraction , compound the unclear peak which

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identification it is not possible was detected, but these the sintering temperature 1000* are high, because 24 hours and it is long furthermore sintering time this invention example in comparison with 9 and 1 0 etc, it is thought as thething which another phase precipitated.

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In addition, as shown in Table 1 and Figure 3 , sintering temperature the;al-LIALO (2) with the;ga -LIALO both phases of (2) had formed 600 *concerning thing (this invention Example 8).

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[0064]

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this way, making use of sol-gel method which utilizes aluminum alkoxide , byfact that it calcines 2 hours or more with low temperature of 600 *or below , the;al-LIALO it became clear for composition which contains (2) to beacquired.

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Especially, sintering temperature 200 * - 550 * with by fact that it does,the;al -LIALO it became clear for composition which contains only (2)to be acquired.

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Furthermore, sintering temperature 600 * with by fact that it does, the;al-type and it became clear for composition where the;ga -type containslialo (2) of both to be acquired.

□0065□

[0065]

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In addition, as shown in Table 1 , the;al -type LIALO composition of(2) single phase as for synthesizable maximum Li /Al mole ratio with (this invention Example 1 7) under approximately 1.7,the;ga -type LIALO composition of (2) single phase as for synthesizable maximum Li /Al mole ratio is 1.3 or less (this invention example 15).

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As Li /Al mole ratio becomes large, it can recognize tendency where sintering time in order to obtain single phase becomes long.

□0066□

[0066]

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In addition, composition of this invention Example 5 and X-ray diffraction result of composition of Comparative Example 9 are shown in Figure 4 .

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Al (2) diffraction peak of O (3) is detected. Li (2) CO (3) with aluminum oxide As for this invention Example 5 and Comparative Example 9, sintering condition 500 * with 12 hours and is identical condition , but lithium carbonate which is a starting material regarding Comparative Example 9

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With this invention Example 5 which on one hand, is synthesized with sol-gel method ,the;al -LIALO as for compound other than (2) what it is notdetected.

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Therefore according to manufacturing method of this invention , composition where the impurity is little can be acquired.

[0067]

Furthermore, composition of this invention Example 5 and X-ray diffraction result of composition of Comparative Example 10 are shown in Figure 5 .

As for this invention Example 5 and Comparative Example 10, sintering condition 500 * with 12 hours and is identical condition , but the;al -LIALO the;be -LIALO (2) is formed to otherthan (2) regarding Comparative Example 10 where addition quantity of water islittle.

On one hand, quantity of water is not detected with sufficient this invention Example 5 ,the;al -LIALO as for compound other than (2) what.

Therefore regarding manufacturing method of this invention , the;be -LIALO there arenot times when (2) forms by adding water to fully , they canacquire composition where impurity is little.

[0068]

(Working Example 2)

It designated composition which is synthesized with Working Example 1 as the positive electrode active material , in this it mixed acetylene black at ratio of 10 mass % as conductor ,it threw this blend , to N-methyl-pyrrolidone solution which melts polyvinylidene fluoride and made the slurry .

this slurry , with doctor blade method application was done next on aluminum foil of the thickness 20;mu m , furthermore N-methyl-pyrrolidone adding heat removal was done.

positive electrode was produced this way.

You inserted in test cell canister with state which repeats separator and metallic lithium foil (negative electrode) which consist of positive electrode and porous polypropylene which itacquires you produced test cell furthermore by pouring liquid doing the nonaqueous electrolyte .

Those which in order to become concentration of 1 mole/liter , melt Liclo (4)were used. In nonaqueous electrolyte , in mixed solvent of ethylene carbonate 50volume % and diethyl carbonate 50volume % lithium perchlorate

[0069]

Until first per positive electrode active material (composition) with constant current density of 50 mA/g 4.3 V ago,concerning test cell which it produces, it charged, after that per positive electrode active material with constant current density of 50 mA/g discharged to 3.0 V.

It shows in Table 1 with discharge capacity at time of this as the initial discharge capacity .

[0070]

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Way it shows in Table 1 , the;al -LIALO in case of composition whichincludes only (2), initial discharge capacity of approximately 470 mAh/g is shownwith maximum and (this invention Example 5), the;ga -LIALO in case of composition whichincludes only (2), initial discharge capacity of approximately 300 mAh/g is shownwith maximum , (this invention example 10), The;al -type and in case of composition to which the;ga -type includeslialo (2) initial discharge capacity of approximately 380 mAh/g was shown with the maximum , (this invention Example 8).

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As for these values, it understands that it is a high capacity in comparisonwith approximately 130 mAh/g of conventional Li CoO (2) type.

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In addition, from result of Table 1 , the;al -LIALO in case of (2)when Li/Al ratio 0.5 - 1.66, the;ga -LIALO it is a (2), it is thoughtthat charge-discharge (Insertion and elimination reaction for composition of lithium ion) is done in 0.5 - 1.25 ranges.

□0071□

[0071]

(□□□□)

(Working Example 3)

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Other than thing which designates average particle diameter of composition as 1 -24;mu m test cell was drawn up with as similar to theabove-mentioned Working Example 2, initial discharge capacity was measured with same condition as Working Example 2.

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Result is shown in Table 2 .

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Way it shows in Table 2 , the;al -type , the;ga -type in case ofwhich, when average particle diameter is smaller than 20;mu m , it understands that initial discharge capacity becomes large in comparison with conventional Li CoO (2) (initial discharge capacity 130 mAh/g).

□0072□

[0072]

□□2□

[Table 2]

□0073□

[0073]

Li/Al モル比	焼成条件		生成相	平均粒径 (μm)	初期放電容量 (mAh/g)	
	焼成温度 (℃)	保持時間 (時間)				
1.0	500	12	α-$LiAlO_2$	1	470	本発明例 5
1.0	500	12	α-$LiAlO_2$	7	440	本発明例 19
1.0	500	12	α-$LiAlO_2$	14	350	本発明例 20
1.0	500	12	α-$LiAlO_2$	23	70	比較例 7
1.0	1000	12	γ-$LiAlO_2$	1	300	本発明例 10
1.0	1000	12	γ-$LiAlO_2$	8	250	本発明例 21
1.0	1000	12	γ-$LiAlO_2$	16	170	本発明例 22
1.0	1000	12	γ-$LiAlO_2$	24	50	比較例 8

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(Working Example 4)

OC (2) H (6) (3) respectively, with aluminum ethoxide and lithium nitrate wasthrown in ethanol , other than thing which is made condition which shows sintering condition in Table 3 composition was acquired with assimilar to Working Example 1. Y OC (2) H (6) (3) with yttrium ethoxide Co cobalt ethoxide

test cell was produced concerning composition which it acquires, tosimilar to above-mentioned Working Example 2, with same condition as Working Example 2 charge-discharge was done to 10 cycle .

And it measured discharge capacity after initial discharge capacity and 10 cycle , measured also degradation ratio of discharge capacity to 10 cycle from initial stage .

Result is shown in Table 3 .

To other than sintering condition and discharge result , it showed also composition formula of the composition in Table 3 .

Way it shows in Table 3 , the;al -type , the;ga -type in case ofwhich being attached, degradation ratio greatly improving you understand byadding Co and Y with Al substitution.

Especially;ga it understands that -type degradation ratio is small.

[0074]

[Table 3]

[0075]

結晶相	組成式	放電容量(mAh/g)		劣化率(%)	備考
		初期	10サイクル後		
α型	$LiAlO_2$	470	350	26	焼成温度 500℃ 保持時間 12 時間 粒径 1μm 以下
α型	$LiAl_{0.9}Co_{0.1}O_2$	450	400	11	
α型	$LiAl_{0.9}Y_{0.1}O_2$	430	410	5	
γ型	$LiAlO_2$	300	250	17	焼成温度 1000℃ 保持時間 12 時間 粒径 1μm 以下
γ型	$LiAl_{0.9}Co_{0.1}O_2$	290	270	7	
γ型	$LiAl_{0.9}Y_{0.1}O_2$	280	280	0	

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(Working Example 5)

Throwing graphite as negative electrode active material , to N-methyl-pyrrolidone solution which melts polyvinylidene fluoride ,it made slurry , with doctor blade method application did this slurry on copper foil of thickness 20;mu m , it produced positive electrode furthermore by adding heat removal doing N-methyl-pyrrolidone .

Furthermore metallic lithium foil was stuck to surface of negative electrode .

Next, this invention Example 5 in Table 1 (;al -type) and other than thing which uses composition of this invention example 10 (;ga -type) positive electrode was produced with as similar to Working Example 2.

test cell was drawn up and, making use of these negative electrode and positive electrode ,to similar to Working Example 2.

With same condition as Working Example 2 charge-discharge was done to 10 cycle vis-a-vis test cell which it acquires, discharge capacity of 10 cycle later wasmeasured.

As a result, with test cell which uses composition of this invention Example 5 (;al -type), the discharge capacity of 10 cycle later showed 300 mAh/g .

In addition concerning test cell which uses composition of this invention example 10 (;ga -type),discharge capacity of 10 cycle later showed 230 mAh/g .

this way, by fact that negative electrode which sticks metallic lithium foil isused, lithium inserting in positive electrode active material , positive electrode active material Li content improves, itunderstands that high discharge capacity is shown even with when charge-discharge cycle wasrepeated.

□0076□

[0076]

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(Working Example 6)

Next, this invention Example 5 in Table 1 (;al -type) and composition of this invention example 10 (;ga -type)

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wasmixed, in order for composition ratio of composition of this invention example 10 (;ga -type) to becomerange of 0 - 100 mass % , other than thing which uses positive electrode active material which was adjusted positive electrode was produced with as similar to the Working Example 2.

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And, making use of these positive electrode test cell was produced to similar toabove-mentioned Working Example 2, with same condition as Working Example 2 charge-discharge was done to 10 cycle .

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And discharge capacity after initial discharge capacity and 10 cycle was measured, degradation ratio (cycle degradation rate)of discharge capacity to 10 cycle was sought.

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Result is shown in Figure 6 .

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As shown in Figure 6 , when the;ga -type content exceeds 20 mass % ,cycle degradation rate becomes 20% or lower , it understands that cycle property which issuperior is shown.

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[0077]

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[Effects of the Invention]

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As above, explained in detail, as for lithium secondary battery of this invention , the;al-type or being something which uses composition to which the;ga -type includes lialo (2) crystal of any one or both as positive electrode active material , as for the this composition atomic weight to be small in comparison with lithium composite oxide of conventional Co typeor Mn type, at same time electrochemical equivalent of lithium equality to the conventional lithium composite oxide above that, It is something where energy density per weight is high.

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It is possible to raise energy density by fact that this composition is usedfor lithium secondary battery .

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[0078]

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In addition, portion of Al in Lialo (2) crystal by factthat it substitutes in element m or element l, it is possible, canimprove from charge-discharge cycle property furthermore to raise stability of crystal structure ofLialo (2) crystal .

□0079□

[0079]

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In addition as for lithium secondary battery of this invention , carbon powder is included asaforementioned negative electrode active material , at same time can install metallic lithium in surface and it can have negative electrode which becomes, being somethingwhere initial discharge is done after battery assembly and becomes, according to this lithium secondary battery , It is possible to insert in composition which by fact that initial charging it does metallic lithium which is installed in negative electrode includes Lialo(2) crystal lithium content of this said composition improves because of this, it ispossible to raise charge-discharge capacity .

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[0080]

In addition manufacturing method of positive electrode active material for lithium secondary battery of this invention ,reacting, designates aluminum alkoxide and lithium compound and water as the dried matter of gel , obtains positive electrode active material which contains Lialo (2) crystal by fact that this dried matter is calcined, 200 * - 600 * itcalcines relatively low temperature by fact that with manufacturing method , it is possiblewith so-called sol-gel method , to make sintering temperature low, The;al -LIALO (2) crystal can be synthesized.

Especially, the;al which synthesis makes difficult from until recentlyby designating sintering temperature as 200 *or higher 550* or below , -LIALO composition whichincludes only (2) crystal can be acquired.

[Brief Explanation of the Drawing(s)]

[Figure 1]

oblique view . which shows one example of lithium secondary battery which is a embodiment of the this invention

[Figure 2]

oblique view . which shows principal part of lithium secondary battery which is shownin Figure 1

[Figure 3]

Figure which shows result of X-ray diffraction of composition of the this invention Example 5 , 8, 10 and 11.

[Figure 4]

Figure which shows result of X-ray diffraction of composition of the this invention Example 5 and Comparative Example 9.

[Figure 5]

Figure which shows result of X-ray diffraction of composition of the this invention Example 5 and Comparative Example 10.

[Figure 6]

The;ga per positive electrode active material -LIALO it is a graph which shows relationshipbetween content and cycle degradation rate of composition which includes (2) crystal .

[Explanation of Symbols in Drawings]

6

sealing plate

5

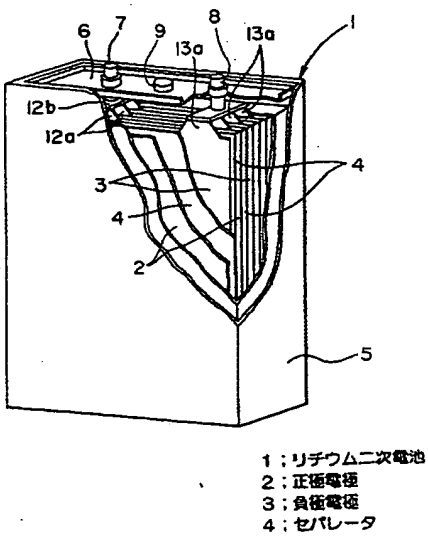
battery case

4

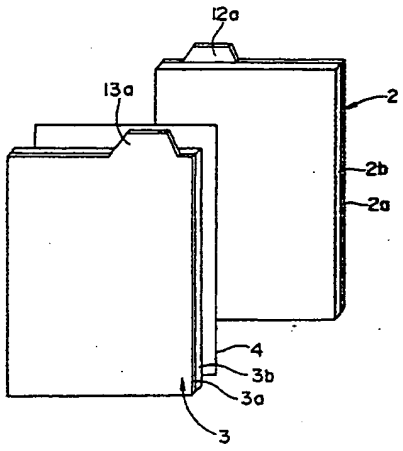
□□□□□	separator
3b	3b
□□□□□	negative electrode film
3a	3a
□□□□□	negative electrode collector
3	3
□□□□	negative electrode
2b	2b
□□□□□	positive electrode membrane
2a	2a
□□□□□	positive electrode collector
2	2
□□□□	positive electrode
1	1
□□□□□□□□	lithium secondary battery

Drawings

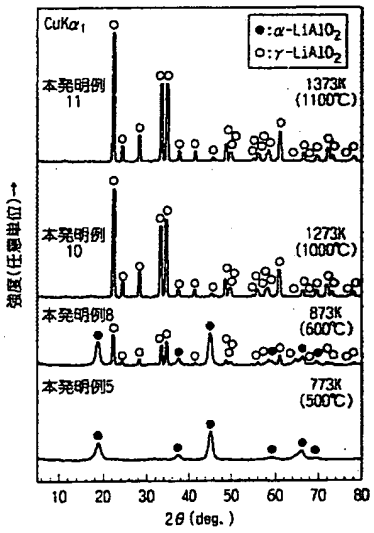
□□1□ [Figure 1]



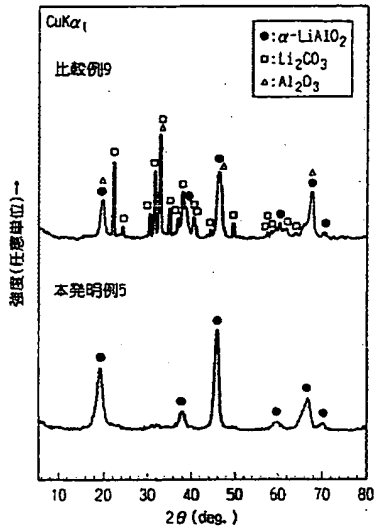
□□2□ [Figure 2]



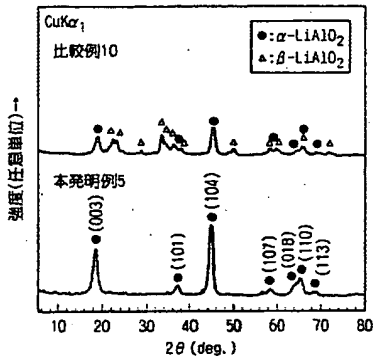
□□3□ [Figure 3]



□□4□ [Figure 4]



□□ 5□ [Figure 5]



□□ 6□ [Figure 6]